DESCRIPTION

GLASS AND GLASS SUBSTRATE HAVING HIGH DIELECTRIC CONSTANT

Technical Field

The present invention relates to a glass having a high dielectric constant and low dielectric loss, preferable as a substrate for electric circuit such as a substrate for high frequency circuit element and flat panel display and the like and a dielectric material.

Background Art

It has entered advanced information age as represented by mobile communication, cell phones, satellite broadcasting, satellite communication, CATV and the like, and the communication tends to be performed faster and higher frequency. Furthermore, according to a requirement for the miniaturization of these equipments, the miniaturization of the circuit elements also has been strongly required.

The size of a circuit element for microwave is based on the wavelength of an electromagnetic wave used. An electromagnetic wave transmitting in a dielectric material having a dielectric constant of (ε) has a wavelength (λ) represented by $\lambda=\lambda_0/(\varepsilon^{1/2})$ where λ_0 represents the wavelength in vacuo. Therefore, since the size of the circuit becomes

small in inverse proportion to square root of ε, a material having high dielectric constant has been required.

Further, relating to a display substrate such as PDP, glass for electric substrate having low alkaline content and high dielectric constant applicable for one having high density, high brightness and low electric consumption is desired. When the dielectric material is used as a capacitor in high frequency and high electric field, the material is required to have large quality constant Q. Since Q is rendered by the relational expression of $Q=1/\tan \delta$ ($\tan \delta$: dielectric loss), a material having low dielectric loss is required.

Conventionally, borosilicate glass containing large amount of PbO component is known as a glass having comparatively high dielectric constant as described above. For example, SiO_2 - RO (R is a alkaline-earth metal) - $(TiO_2+ZrO_2+SnO_2)$ - PbO system glass is disclosed in Tokukaihei-3-297008A, and SiO_2 - PbO - Al_2O_3 system glass is disclosed in Tokukaihei-4-16527A and Tokukaihei-4-108631A.

It is to be noted that P_2O_5 - B_2O_3 - Nb_2O_5 system glass is known as an optical glass having high refractive index (Tokukaisho-52-132012A and Tokukaihei-8-104537A, etc.). However, the glass containing no PbO component is required in an environmental viewpoint.

However, since this glass contains large amount of alkaline, it has low resistance property to voltage because

of high mobility thereof. Therefore, it is not suitable
for a substrate of a high frequency circuit element and
electric circuit.

The object of the present invention is to provide a
material suitable as a substrate for such as a high
frequency circuit element, display and the like, where the
material is a glass having high dielectric constant, low
dielectric loss and comparatively low alkaline content, in
which the defects seen in the above-described earlier
development is totally improved.

Disclosure of Invention

The present inventors has studied and researched in
order to achieve the above-described object, and finally
has found that the glass substrate has a remarkably high
dielectric constant and low dielectric loss in P_2O_5 - RO (R
is alkaline metal earth) - Nb_2O_5 system glass having a
composition within specific range, which has not been
disclosed concretely in prior art. Thus the present
inventor has accomplished the invention.

That is, according to the first aspect of the
invention, the glass of the present invention comprises
following components by mass%.

P_2O_5	5-25%
BaO+SrO	21-50%
Nb_2O_5	35-65%

Li$_2$O+Na$_2$O+K$_2$O   0-3%

The glass of the present invention preferably comprises following components by mass%.

P$_2$O$_5$	5-25%
B$_2$O$_3$	0-15%
SiO$_2$+GeO$_2$	0-5%
BaO+SrO	21-50%
MgO+CaO	0-25%
Nb$_2$O$_5$	35-65%
TiO$_2$	0-15%
Ta$_2$O$_5$	0-15%
Bi$_2$O$_3$	0-15%
ZnO	0-15%
WO$_3$	0-15%
Y$_2$O$_3$+La$_2$O$_3$+Gd$_2$O$_3$	0-15%
Li$_2$O+Na$_2$O+K$_2$O	0-3%
Al$_2$O$_3$	0-5%
Sb$_2$O$_3$	0-0.5%

The glass more preferably comprises following components by mass%;

P$_2$O$_5$	5-20%
B$_2$O$_3$	0-10%
SiO$_2$+GeO$_2$	0-5%
BaO	21-50%
MgO+CaO	0-25%
Nb$_2$O$_5$	35-65%

TiO_2	0-15%
Ta_2O_5	0-15%
Bi_2O_3	0-15%
ZnO	0-15%
WO_3	0-15%
$Y_2O_3+La_2O_3+Gd_2O_3$	0-15%
$Li_2O+Na_2O+K_2O$	0-3%
Al_2O_3	0-5%
Sb_2O_3	0-0.5%

wherein $Nb_2O_5/(BaO+SrO)$ is 0.85-2.20.

It is preferable that the glass of the invention is substantially free from PbO component and has a dielectric constant of 15 or more. Further, the glass preferably has a dielectric loss of 10.0×10^{-4} or less and an electrical resistivity of 1.0×10^{16} $\Omega \cdot cm$ or more.

According to the second aspect of the present invention, the glass substrate of the present invention consists of the above-described glass of the first aspect.

Best Mode for Carrying Out the Invention

The following is the reason for limiting the composition of the individual components as described above.

That is, P_2O_5 component is an important material as a glass forming oxide, and preferably is contained 5% or more in order to obtain a stable glass having no devitrification. Further, in order to sustain a high dielectric constant,

P_2O_5 content is 25% or less, preferably 22% or less and particularly preferably 20% or less.

B_2O_3, SiO_2 and GeO_2 components act as glass forming oxides, and are effective in stabilizing the glass. Total content of B_2O_3, SiO_2 and GeO_2 is preferably 0.5% or more and more preferably 1.5% or more. B_2O_3 component is preferably 0.5% or more and more preferably 1.5% or more. However, in order to sustain high dielectric constant, B_2O_3 content is preferably 15% or less and more preferably 10 % or less. Total content of SiO_2 and GeO_2 components are preferably 5% or less, more preferably 3% or less and particularly preferably 1% or less.

SrO and BaO components are effective in increasing a dielectric constant of the glass. Total content of these components are preferably 21% or more and 50% or less, and more preferably 25% or more and 40% or less. Further, BaO content is preferably 21% or more and more preferably 25% or more.

MgO and CaO components are effective in inhibiting a devitrification of the glass. In order to sustain a high dielectric constant, total content of these components are preferably 25% or less, more preferably 10% or less, and particularly preferably 5% or less.

Nb_2O_5 component is effective in improving a dielectric constant. Nb_2O_5 content is preferably 35% or more, and from the viewpoint of resistance to

devitrification property, preferably 65% or less, more preferably 60% or less and particularly preferably 55% or less. Further, in order to increase a dielectric constant and sustain a stability of the glass, the value of $Nb_2O_5/(BaO+SrO)$ is preferably in the range from 0.85 to 2.2, and more preferably from 0.95 to 1.8.

TiO_2, Ta_2O_5, Bi_2O_3, ZnO, WO_3, Y_2O_3, La_2O_3 and Gd_2O_3 components are effective in increasing a dielectric constant. However, from the viewpoint of resistance to devitrification property, these components are preferably 15% or less. Especially, total content of Y_2O_3, La_2O_3 and Gd_2O_3 is preferably 15% or less.

Li_2O, Na_2O and K_2O components improve a melting property of the glass. However, alkaline ions have extremely high mobility in the glass so that an electrical resistivity is reduced. Deposition of alkaline components and dielectric breakdown possibly occur under high voltage, the glass preferably contains individual components of 3% or less in total amount and more preferably free from these components.

Al_2O_3 component is effective in improving chemical durability of a glass. From the viewpoint of resistance to devitrification property, Al_2O_3 content is preferably 5% or less.

Sb_2O_3 component is effective as a refining agent. It is enough that the content of Sb_2O_3 component is 0.5% or

less.

The glass of the invention is preferably free from PbO and As_2O_3 components which are environmentally harmful.

It is to be noted that other components such as Rb_2O, Cs_2O, TeO_2, CeO_2, SnO components and the like can be added to the glass of the invention within about 5% in total content, if necessary.

It is preferable that the glass and glass substrate of the invention has a dielectric constant of 15 or more, more preferably 16 or more and particularly preferably 17 or more.

The glass and glass substrate of the present invention preferably has electrical resistivity of 1×10^{16} $\Omega \cdot cm$ or more.

Next, compositions of preferable examples of the glass having a high dielectric constant according to the present invention and comparative examples (mass%) are shown in Tables 1 to 7, accompanied with a dielectric constant (ε) and dielectric loss (tan δ) at 25°C and 1MHz, electrical resistivity ($\rho/\Omega \cdot cm$), coefficient of thermal expansion ($\alpha/10^{-7}K^{-1}$) in temperature from 100 to 300°C, refractive index (nd) and Abbe number (νd). In the Tables, the dielectric constant and dielectric loss were measured by impedance measurement system. The electrical resistivity was measured by a high electrical resistance

meter produced by Hewlett-Packard Co. As for the coefficient of thermal expansion, rod samples (length of 20mm x diameter of 5mm) manufactured by forming the glasses of each example are measured by using a push-rod type thermal dilatometer in temperature from 100 to 300°C.

The examples of glasses according to the invention were obtained by using nitrates, carbonates, phosphates and oxides as the materials thereof, weighing and mixing them, melting and refining them in a platinum crucible at about 1000 to 1500°C for about 2 to 5 hours, stirring to be homogenous, successively being cast to a metal die, and being annealed.

Table 1

	EXAMPLES			
	No.1	No.2	No.3	No.4
SiO_2				1.0
B_2O_3	9.9	3.9	1.9	
P_2O_5	10.0	12.0	12.0	14.1
Al_2O_3				
Na_2O				
K_2O				2.6
BaO	38.0	37.0	33.0	28.7
TiO_2				2.2
Nb_2O_5	42.0	47.0	53.0	51.3
PbO				
Sb_2O_3	0.1	0.1	0.1	0.1
OTHERS				
ε	18.9	21.5	25.2	24.9
$\tan \delta$	8.7×10^{-4}	7.1×10^{-4}	5.7×10^{-4}	6.0×10^{-4}
$\rho/\Omega \cdot cm$	2.5×10^{16}	1.7×10^{16}	1.4×10^{16}	$-$
α/K^{-1}	86×10^{-7}	86×10^{-7}	81×10^{-7}	80×10^{-7}
nd	1.8894	1.9405	1.9878	1.9646
νd	26.2	24.0	22.0	21.6

Table 2

	EXAMPLES			
	No.5	No.6	No.7	No.8
SiO_2				
B_2O_3	1.9	12.9	12.9	9.9
P_2O_5	12.0	7.0	7.0	10.0
Al_2O_3				
Na_2O			2.0	
K_2O		2.0		
BaO	33.0	32.0	32.0	38.0
TiO_2	2.0			
Nb_2O_5	51.0	46.0	46.0	37.0
PbO				
Sb_2O_3	0.1	0.1	0.1	0.1
OTHERS				Bi_2O_3 5.0
ε	25.6	19.1	19.5	18.6
$\tan \delta$	5.6×10^{-4}	6.8×10^{-4}	8.3×10^{-4}	7.5×10^{-4}
$\rho/\Omega \, cm$	—	2.1×10^{16}	2.1×10^{16}	—
α/K^{-1}	82×10^{-7}	83×10^{-7}	86×10^{-7}	85×10^{-7}
nd	1.9938	1.8939	1.8966	1.8832
vd	21.6	24.8	24.9	26.7

Table 3

	EXAMPLES			
	No.9	No.10	No.11	No.12
SiO_2				
B_2O_3	9.9	9.9	9.9	9.9
P_2O_5	10.0	10.0	10.0	10.0
Al_2O_3				
Na_2O				
K_2O				
BaO	38.0	40.0	33.0	33.0
TiO_2				
Nb_2O_5	37.0	35.0	42.0	40.0
PbO				
Sb_2O_3	0.1	0.1	0.1	0.1
OTHERS	Ta_2O_5 5.0	ZnO 5.0	CaO 5.0	SrO 7.0
ε	18.4	17.2	18.6	18.2
$\tan \delta$	7.0×10^{-4}	11.0×10^{-4}	8.7×10^{-4}	8.0×10^{-4}
$\rho/\Omega \cdot cm$	2.0×10^{16}	1.9×10^{16}	–	2.2×10^{16}
α/K^{-1}	86×10^{-7}	82×10^{-7}	86×10^{-7}	84×10^{-7}
nd	1.8789	1.8561	1.8799	1.8729
νd	27.0	29.2	27.3	27.6

Table 4

	EXAMPLES			
	No.13	No.14	No.15	No.16
SiO_2				
B_2O_3	9.9	9.9	9.9	9.9
P_2O_5	13.0	15.0	15.0	20.0
Al_2O_3				
Na_2O				
K_2O				
BaO	35.0	28.0	30.0	25.0
TiO_2				
Nb_2O_5	42.0	47.0	45.0	45.0
PbO				
Sb_2O_3	0.1	0.1	0.1	0.1
OTHERS				
ε	18.6	20.0	19.1	17.9
$\tan \delta$	9.0×10^{-4}	11.0×10^{-4}	9.0×10^{-4}	9.4×10^{-4}
$\rho / \Omega \cdot cm$	1.8×10^{16}	1.6×10^{16}	–	2.0×10^{16}
α / K^{-1}	81×10^{-7}	79×10^{-7}	82×10^{-7}	78×10^{-7}
nd	1.8737	1.8901	1.8791	1.8544
vd	26.0	23.6	24.5	24.4

Table 5

	EXAMPLES			
	No.17	No.18	No.19	No.20
SiO_2				
B_2O_3	9.9	9.9	1.9	9.9
P_2O_5	10.0	10.0	10.0	10.0
Al_2O_3		5.0		
Na_2O				
K_2O				
BaO	38.0	38.0	33.0	33.0
TiO_2			2.0	
Nb_2O_5	37.0	37.0	51.0	42.0
PbO				
Sb_2O_3			0.1	0.1
OTHERS	Y_2O_3 5.0		GeO_2 2.0	MgO 5.0
ε	17.5	16.0	26.5	19.0
$\tan \delta$	10.0×10^{-4}	12.0×10^{-4}	5.1×10^{-4}	9.0×10^{-4}
$\rho / \Omega \cdot cm$	–	2.5×10^{16}	–	–
α / K^{-1}	81×10^{-7}	80×10^{-7}	83×10^{-7}	83×10^{-7}
nd	1.8695	1.8368	1.9975	1.8850
vd	28.6	28.9	20.7	26.5

Table 6

	EXAMPLES			
	No.21	No.22		
SiO_2				
B_2O_3	9.9	12.9		
P_2O_5	10.0	7.0		
Al_2O_3				
Na_2O				
K_2O		2.0		
BaO	38.0	31.0		
TiO_2				
Nb_2O_5	37.0	46.0		
PbO				
Sb_2O_3		0.1		
OTHERS	La_2O_3 5.0	Li_2O 1.0		
ε	17.9	20.0		
$\tan \delta$	9.7×10^{-4}	8.8×10^{-4}		
α/K^{-1}	81×10^{-7}	89×10^{-7}		
nd	1.8700	1.8992		
νd	29.0	25.3		

Table 7

	COMPARATIVE EXAMPLE			
	No. A	No. B	No. C	No. D
SiO$_2$				
B$_2$O$_3$	24.48	13.44	10.32	6.03
P$_2$O$_5$	44.37	27.24	34.20	28.49
Al$_2$O$_3$				2.41
Na$_2$O				6.19
K$_2$O		16.96	6.84	
BaO				
TiO$_2$				4.38
Nb$_2$O$_5$	31.15	42.36	34.62	52.5
PbO				
Sb$_2$O$_3$				
OHTERS			MgO 6.70 CaO 7.32	
ε	8.6	12.2	11.5	21.12
tan δ	13×10^{-4}	13×10^{-4}	14×10^{-4}	12×10^{-4}
ρ/Ω cm	1.5×10^{13}	3.8×10^{14}	2.8×10^{15}	3.8×10^{12}
α/K^{-1}	41×10^{-7}	87×10^{-7}	74×10^{-7}	54×10^{-7}
nd	–	1.7032	1.6983	1.8482
νd	–	29.2	32.2	–

As shown in Tables 1 to 7, every glass of the examples according to the present invention shows a high dielectric constant, low dielectric loss and high electrical resistivity. Further the glasses are transparent. In the glass of the examples according to the present invention, the coefficient of thermal expansion in temperature from 100 to 300°C is in the range from 80 x 10^{-7} to 86 x 10^{-7}K^{-1}, refractive index (nd) is in the range from 1.83 to 2.00, and Abbe number is from 20.7 to 29.2.

Industrial Applicability

As described above, the glass of the present invention has a specific composition of a P_2O_5 – RO – Nb_2O_5 system glass, shows a high dielectric constant, low dielectric loss and high electrical resistivity, and is useful as substrates for an electric circuit such as a high frequency circuit element, flat panel display and the like and dielectric materials.